

Optimization of Nano-Carbon Materials for Hydrogen Sorption



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The presentation contains no proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: 01 February 2005
- End: 31 January 2010
- 85% complete

Budget

- Total project funding
 - DOE: \$1,065,209
 - Contractor: \$269,181
- Funding for FY08 \$235,000
- Funding for FY09 \$235,000

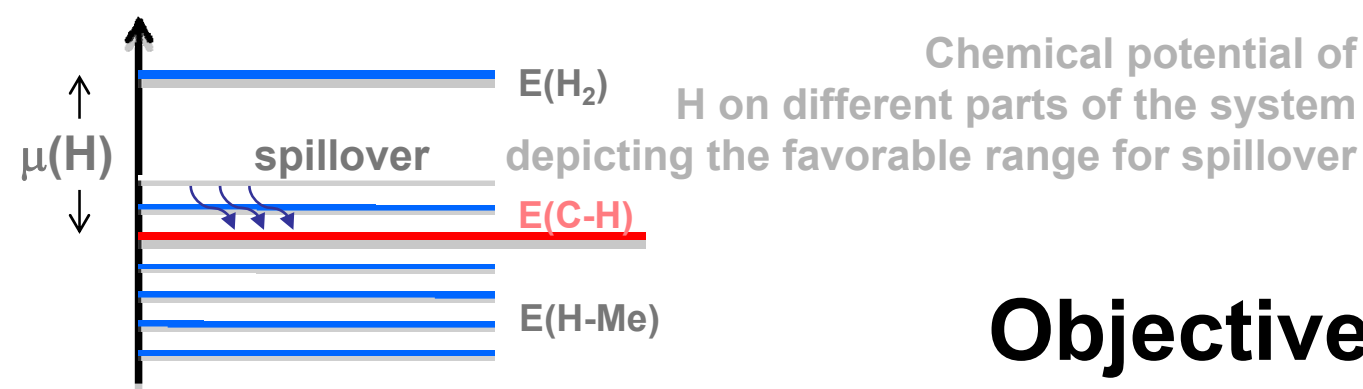
Barriers

Barriers to be addressed

- A** -- System weight and volume
- E** -- Charging/discharging rates
- P** -- Lack of understanding of hydrogen physisorption

Partners

NREL, Air Products Corp, NIST, U Michigan, Caltech, regular teleconferences, face-to-face meetings (Houston, Golden, CO, Washington, Gaithersburg, ORNL TT, MRS meetings).



Objectives-Relevance

OVERALL: Model materials structures' interaction with hydrogen, optimize their makeup for storage and assess the volumetric and gravimetric capacity. Recommend the synthetic goals (e.g. pore/channel size, metal enhancement routes).

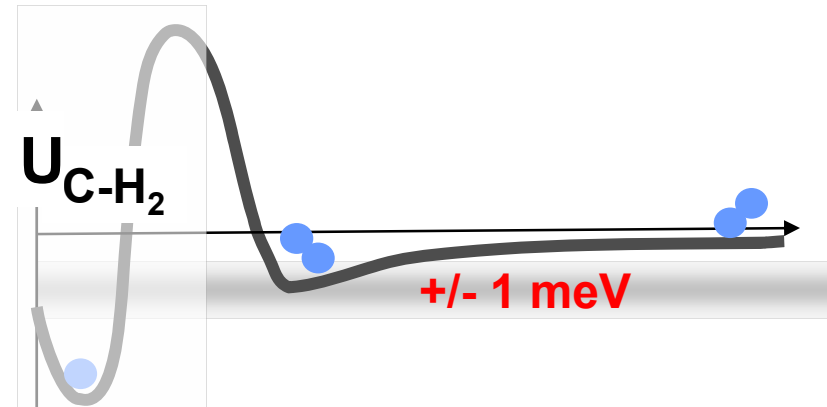
2008:

- Identify the obstacles (thermodynamics and kinetic) for the spillover and suggest/design the materials to overcome them
- Explore doping as an anchor to metal cluster, effect of dopants on spillover threshold
- Estimate the volumetric and gravimetric capacities of foam-family and NT-bundles
- **Synthesis of metal- and electronegative-group- (F , BF_3) enhanced VANTA (vertically aligned nanotube arrays, *contrast to fibers*) for H_2 adsorption.**

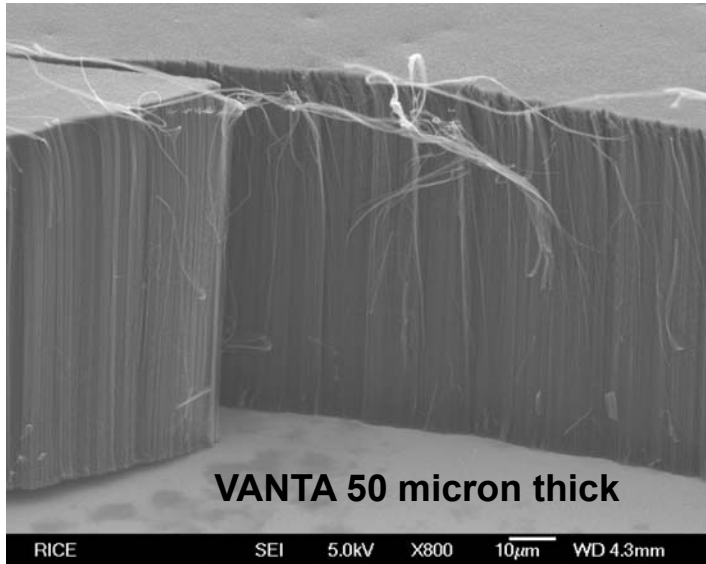
2009:

- continue the above and
- **Assess the effect of impurities and environment on the spillover**
- **Study the conditioning of graphitic substrates, by adding O, B, and organic molecules**
- **Study possibility of H atom diffusion on graphitic receptors**
- **Complete experiments with electronegative-group (F , BF_3) enhancement**
- **Sorption on foams, and novel B-structures including metallacarborane-MOFs**

APPROACH



the potential depths obtained from experiment (weaker) and *ab initio* (stronger) differ by 2 meV, affecting the capacity estimates



1 Rapid computation of storage capacity

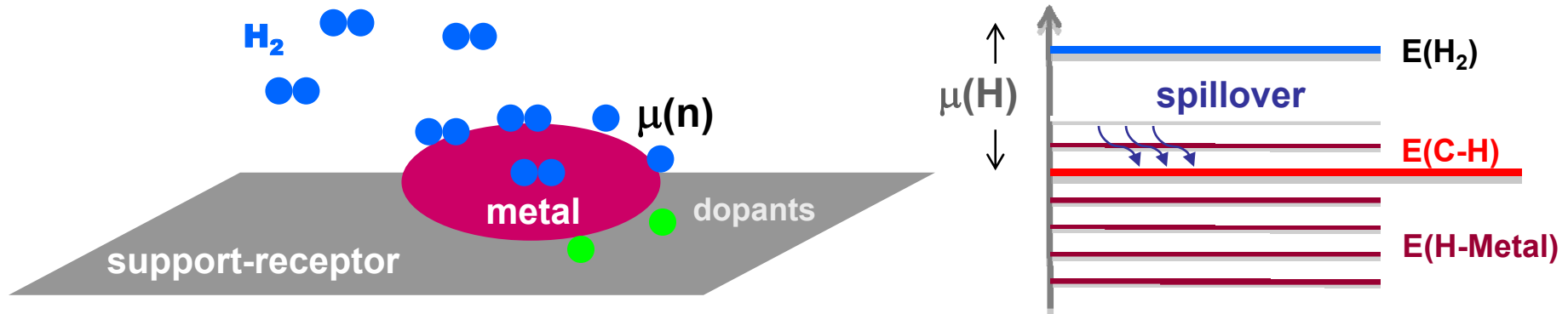
- via Grand Canonical Monte Carlo simulations for structures of interest (90%, cont. 2009)
- judicious choice of potential of paramount importance, perform GCMC with **both** potentials to determine the range for the storage capacity
- consider quantum corrections via Feynman-Hibbs effective field (80%)
- add the similar-foam family analysis (30%)

2 Experimental

- **VANTA** of nitrogen doped C-nanotubes, can be grown in large amounts with CVD methods. The alignment enhances gas transport into the array
- The aligned nature also lends itself to insertion of bulky anions, e.g. **BF₃⁻** as does nitrogen doping. Test same for **AC** (from Channing Ahn, Caltech)

3 Catalytic spillover “nano-thermodynamics”

- Analysis of H-binding energies in the presence of dopants. Compute diffusion barriers for an H atom through DFT calculations. (Role of bridges, defects and dopants and impurities on the overall process of spillover.)



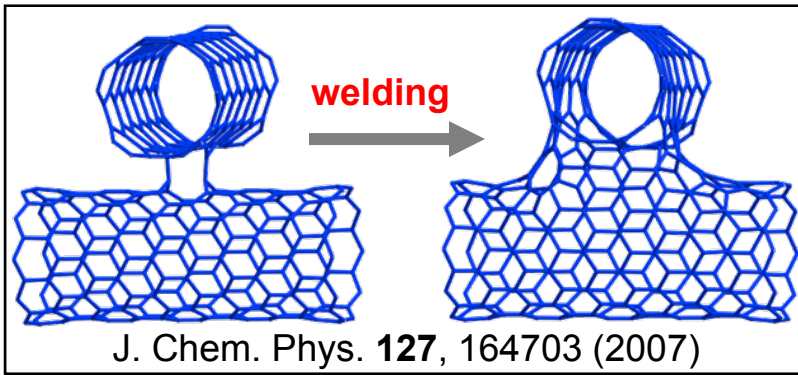
$$\mu(H_2\text{-gas}) > \mu(H@metal) > \mu(H@support)$$

- Identify thermodynamically favorable and kinetically accessible paths. Reconcile strong H binding to Me with possibility of spillover: compare chemical potential of H on metal to that on receptor (90% done, various metals added)
- These steps help in determining the key elements for spillover that can later help designing more efficient systems—support, catalyst, bridges (For FY 2010)

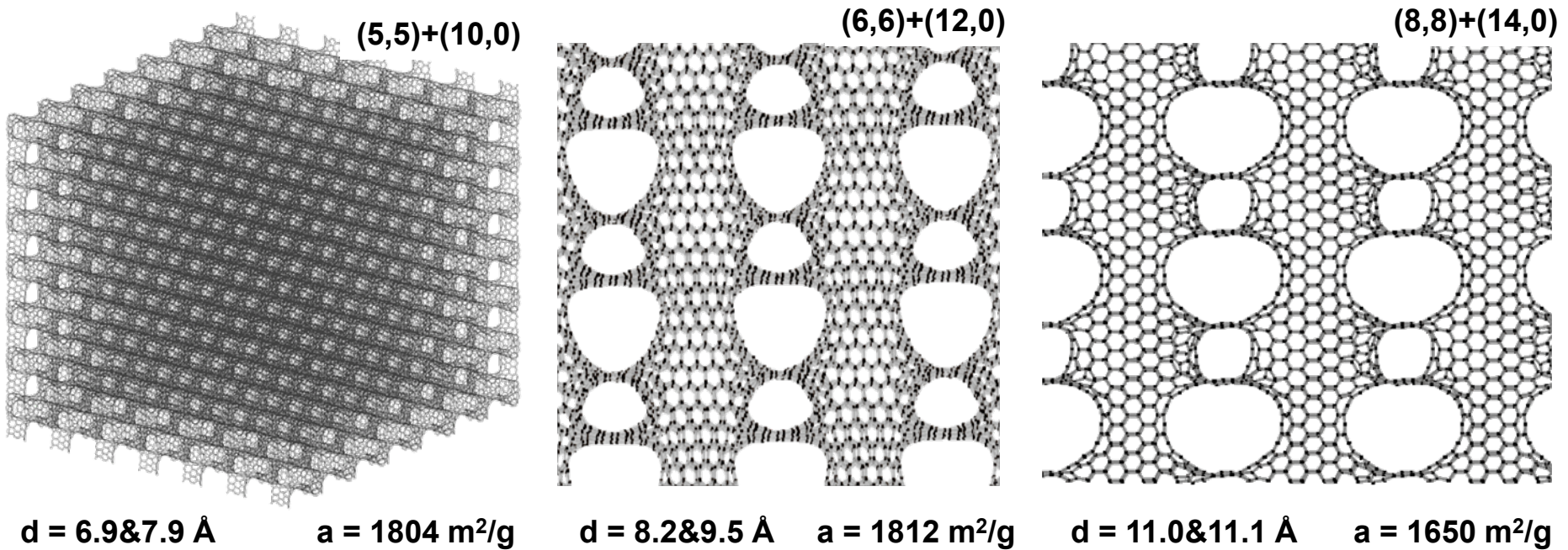
4 Metallocarboranes

- Calculate hydrogen sorption *energies*, identify metal atoms best to adsorb maximum *number* of H₂ (65% done)
- Generate metallocarborane-based MOFs, using semi-empirical methods, and estimate storage capacity at ambient conditions (for FY 2010)

Optimization of H₂ storage in the SWNT-generated foams



By varying separations and diameters, foams with different porosity are generated. Accessible surface is computed with N₂-probe, comparable with the measured by BET.

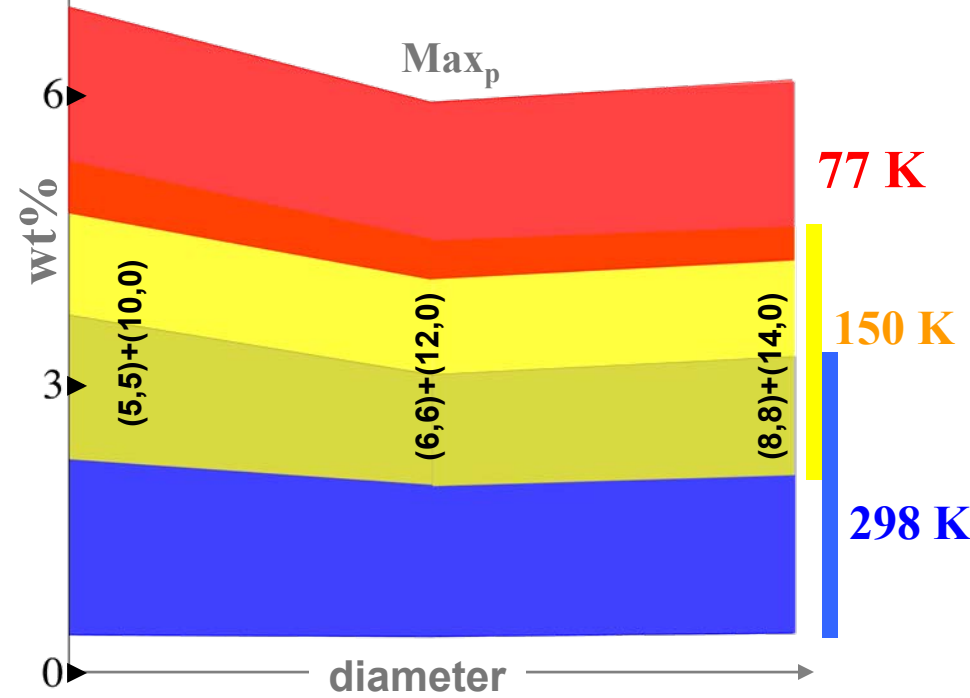
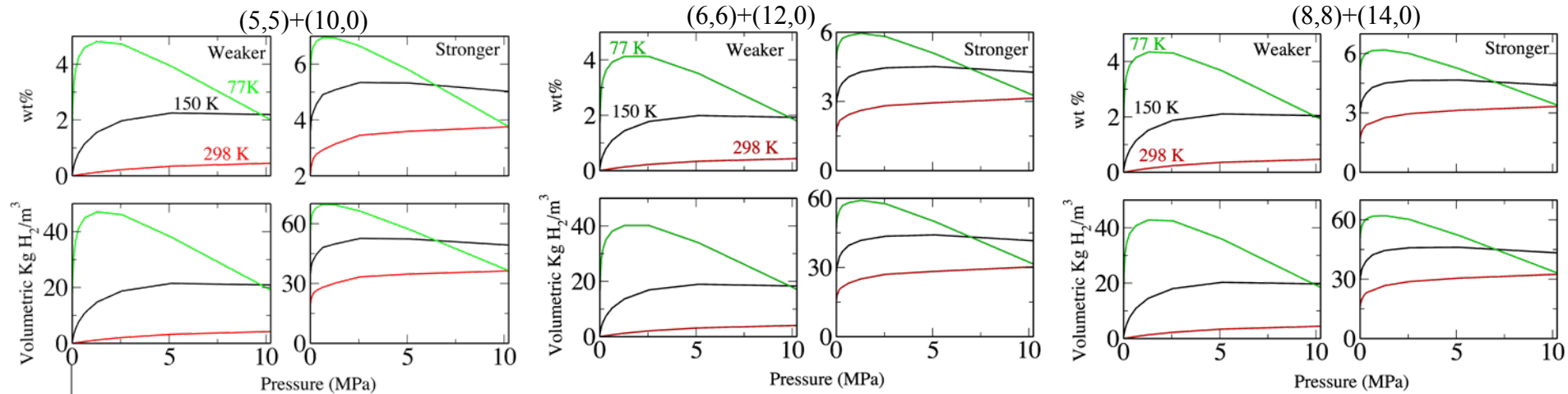


Designed scalable inexpensive carbon foams with optimized porosity for enhanced dihydrogen binding and storage capacity that could meet DOE 2010 targets

Optimization of H₂ storage in foams

technical accomplishments 1

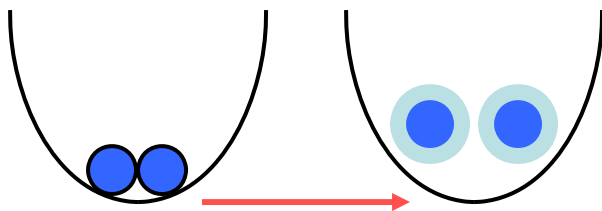
Foams of similar density $\sim 0.9 \text{ gm/cm}^3$ are compared, with *weak* [Wang, 1980] and *strong* [Patchkovskii-Seifert, 2005] potentials, and H₂-H₂ [Silvera-Goldman, 1978]. Storage excess computed



(5,5)+(10,0) foam appears optimum for storage, with pores close to $\sim 3.5 \text{ \AA}$

Calculations indicate that carbon foams with optimized pore structure could have $>60 \text{ g/L}$ and $>6 \text{ wt\%}$ storage capacities at $\sim 77 \text{ K}$. This exceeds DOE 2015 storage targets on a materials basis

Quantum corrections to the foams capacity

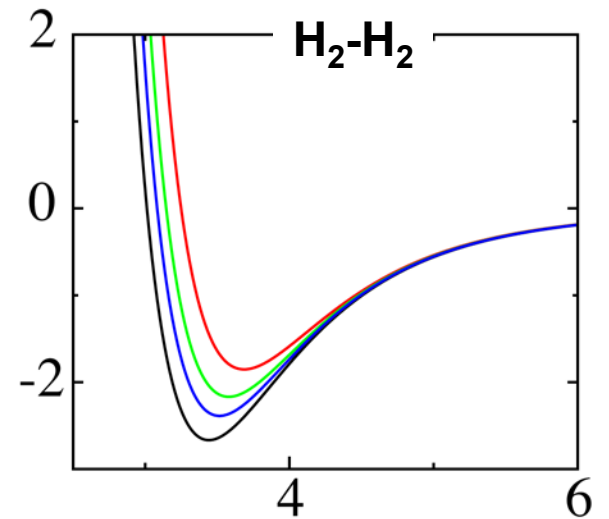
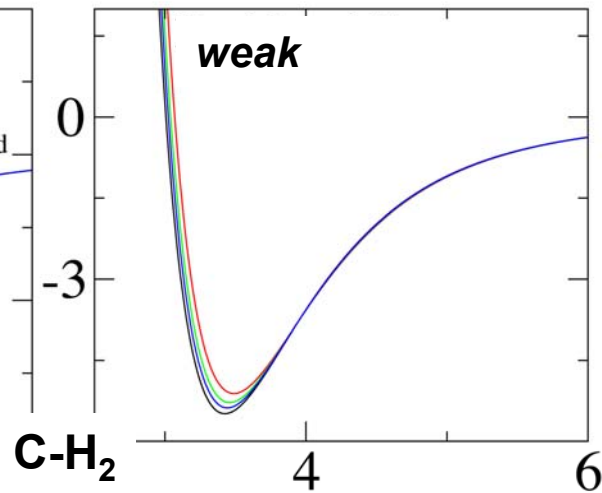
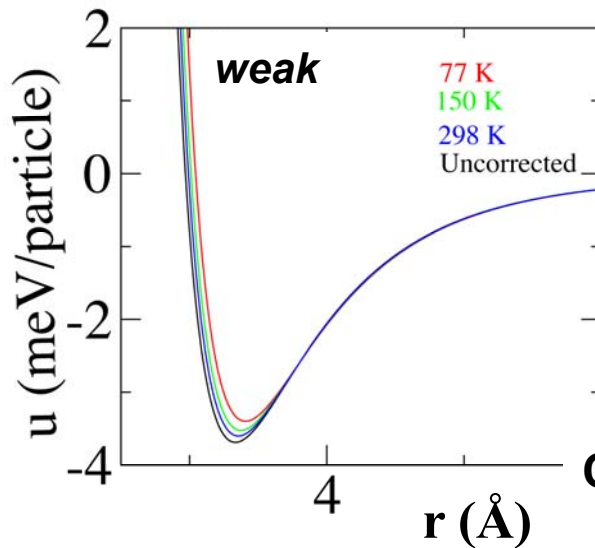


Thermal de Broglie wavelength $\Lambda = \left(\frac{\beta \hbar^2}{2\pi m} \right)^{\frac{1}{2}}$ and criterion $\Lambda/a \ll 1$ $a =$ pore size

depending on temperature, for the foams $\Lambda/a = 0.2 \sim 0.1$

Quantum-fluid molecule as Gaussian wave packet, effective interaction potential

$$U_{FH}(r) = U(r) + \frac{\beta \hbar^2}{24\mu} \left[U''(r) + \frac{2U'(r)}{r} \right]$$



C-H₂ and H₂-H₂ corrections depend on temperature, with the QC in C-H₂ is less significant. **Essentially, quantum corrections add some repulsion**

(5,5)-(10,0) Foam

Quantum corrections effect on storage capacity

Classical overestimates by (%)

T	C-H ₂ with-QC wt% wt total (~10 MPa)	both C-H ₂ and H ₂ -H ₂ with QC wt total	wt excess
298 K	2.6-3.1	5.6-5.8 (10 MPa)	7.8-12
150 K	3.2-4.0	12-13 (~5 MPa)	14-16
77 K	3.1-5.2	18-23 (~1 MPa)	21-24

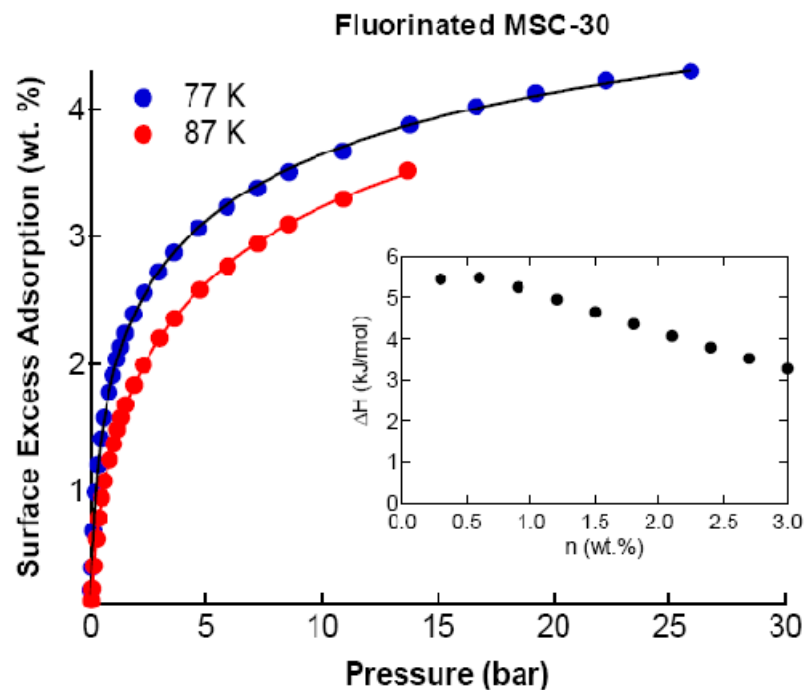
The storage capacities computed without quantum corrections are overestimated

QC for C-H₂ as well as for H₂-H₂ potentials must be accounted for

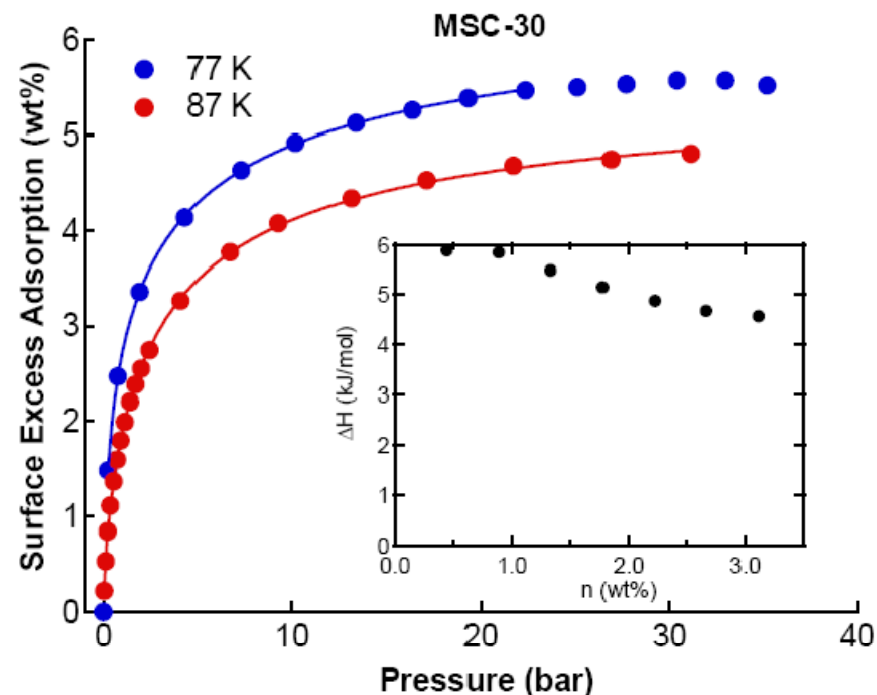
Including quantum corrections is important for accurate comparison with the DOE targets

Experiments on storage in electro-negative-group- (F , BF_3) enhanced VANTA and AC

technical accomplishments 2



Adsorption isotherm of BF_3/F_2 -treated MSC-30 sample at 100 °C, (wt gain 19 %). Inset shows the isosteric heat as a function of surface excess adsorption. Limiting zero-coverage adsorption enthalpy is approximately 6.1 kJ/mol, consistent with that of pristine MSC-30

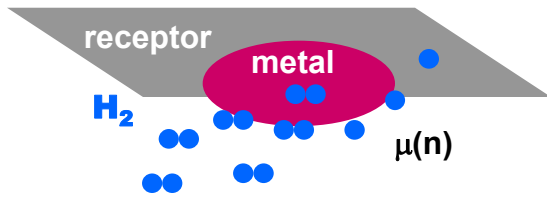


For comparison, the adsorption Isotherm of pure MSC-30 (3350 m²/g). Inset: isosteric heat. The zero-coverage enthalpy for MSC-30 was approximately 6.2 kJ/mole. *Adsorption data provided by Channing Ahn, Caltech*

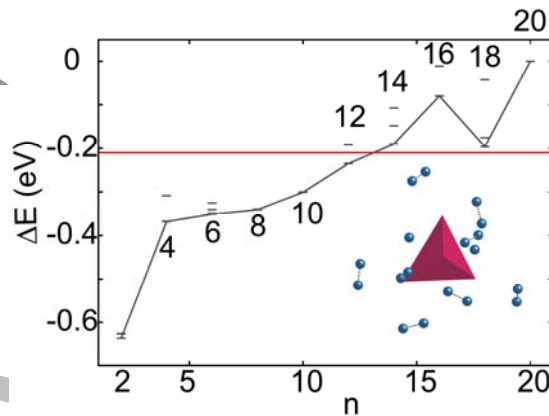
Initial studies suggest that converting a high surface carbon substrate to a superacid with charge separation stabilized via BF_3 complexation needs further testing

technical accomplishments 3

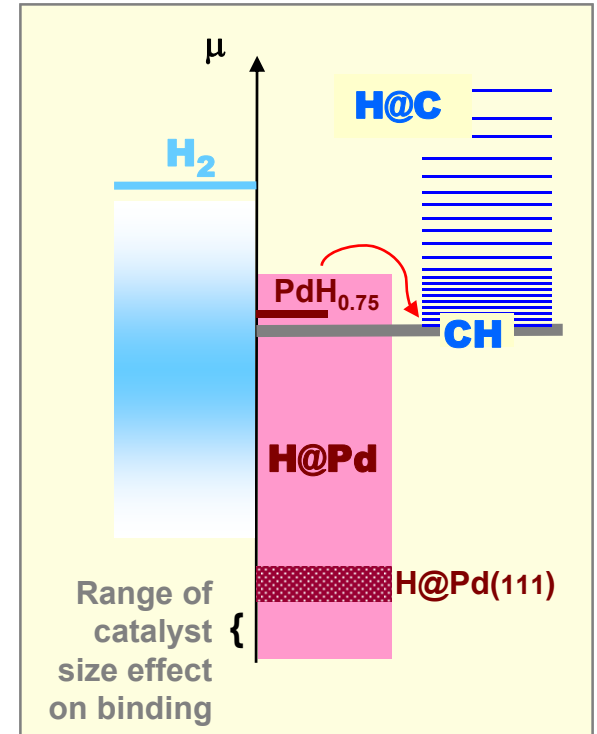
Spillover: Catalyst as a pump



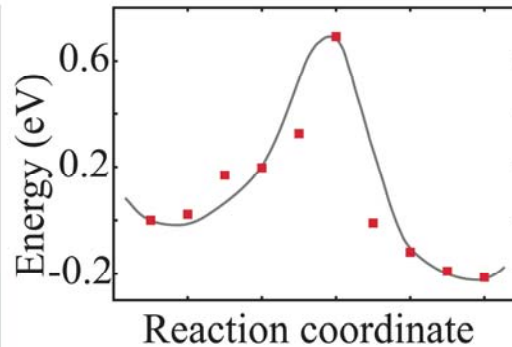
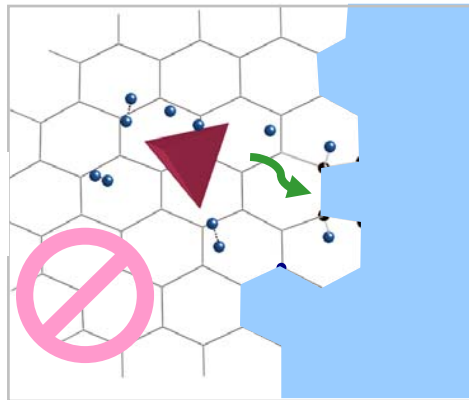
Storage-phase CH and its nucleation barrier identified [Phys Rev B 78 041402-R 2008]



Chemical potential $\mu(n)$ rises with saturation, to permit spillover onto receptor [A. Singh, submitted, 2009]



Observed: Reversible hydrogenation of graphene [Novoselov et al. Science 2009; Brus et al. NL 2008]



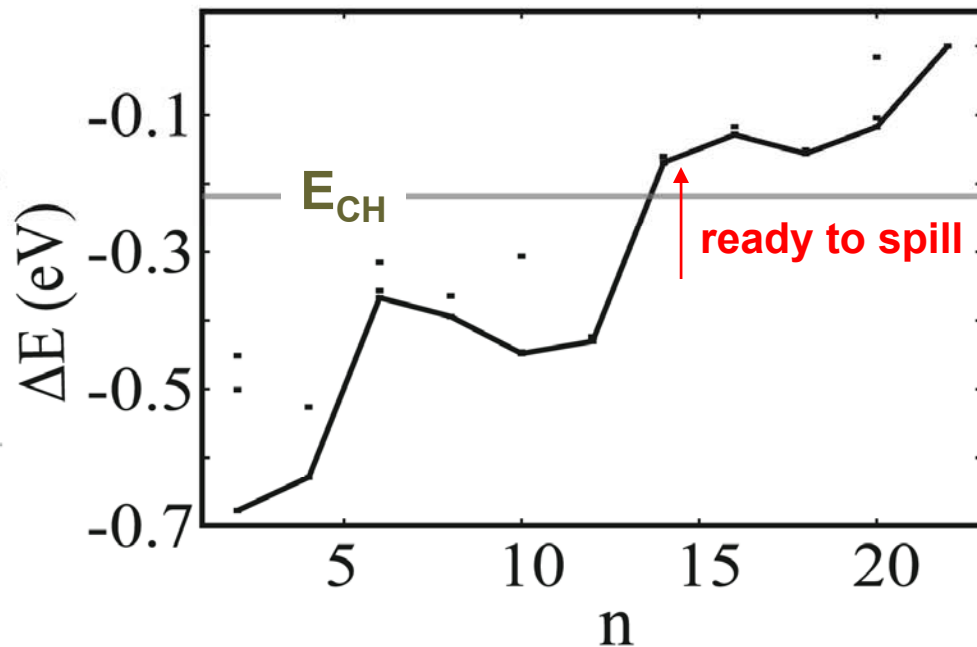
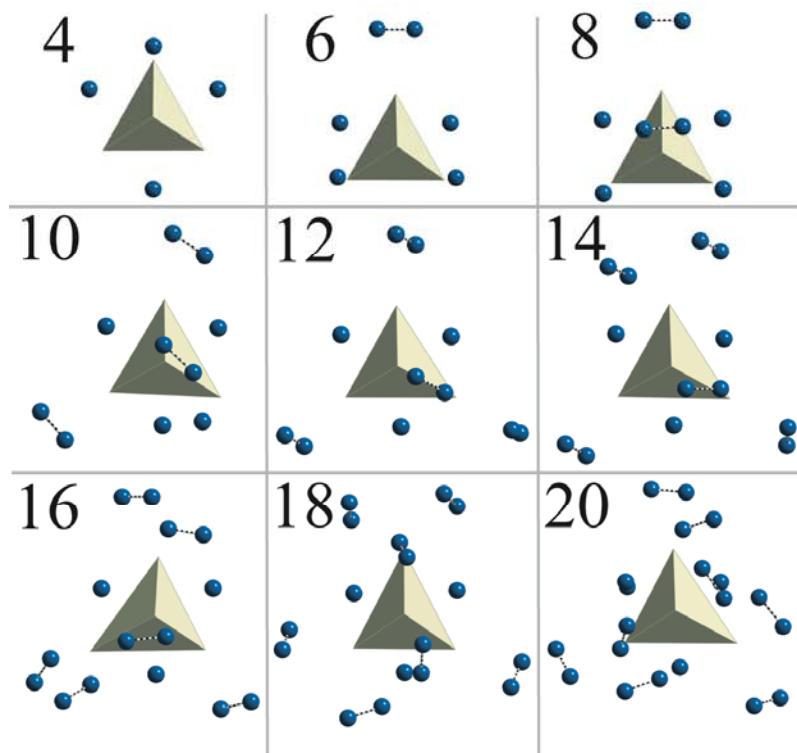
H shows clear affinity towards “storage phase”, and low activation barrier

Computations of binding energies in the key-states— gas, catalyst, storage-phase on the receptor—reveal the internal “machinery” of spillover, reaching up to 7.7 wt% storage, with potential to exceed 2015 DOE goals

Extended catalyst analysis to **Ni** to determine spillover-saturation window

technical accomplishments 3

Find the energy levels for **H** on free **Ni₄**, by selecting the lowest for each **n** and watch for the crossover with the “storage phase” on the receptor



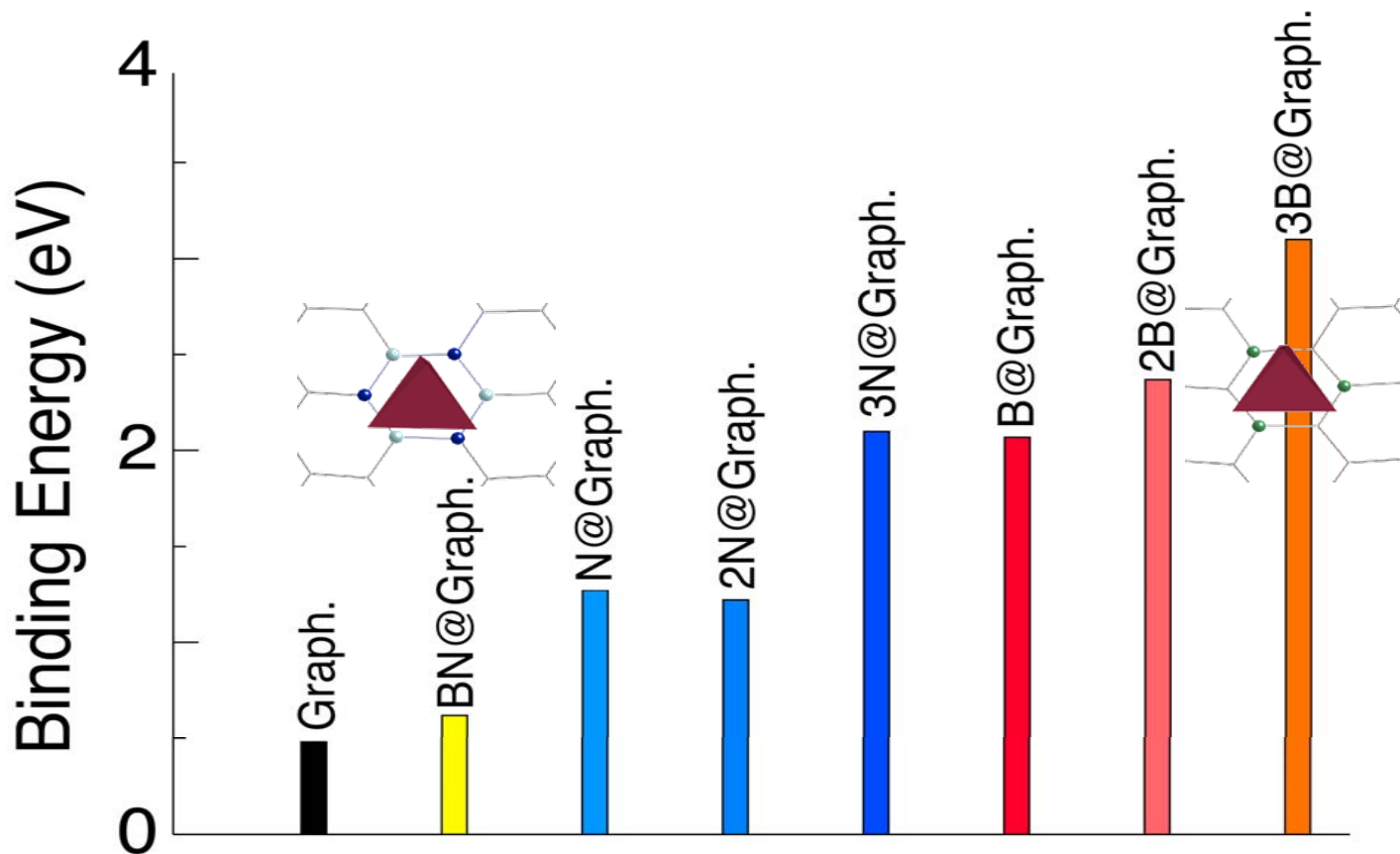
*calculations at 0 K

First two H₂ molecules dissociate; catalyst saturates at n = 20 after adsorbing 10th H₂

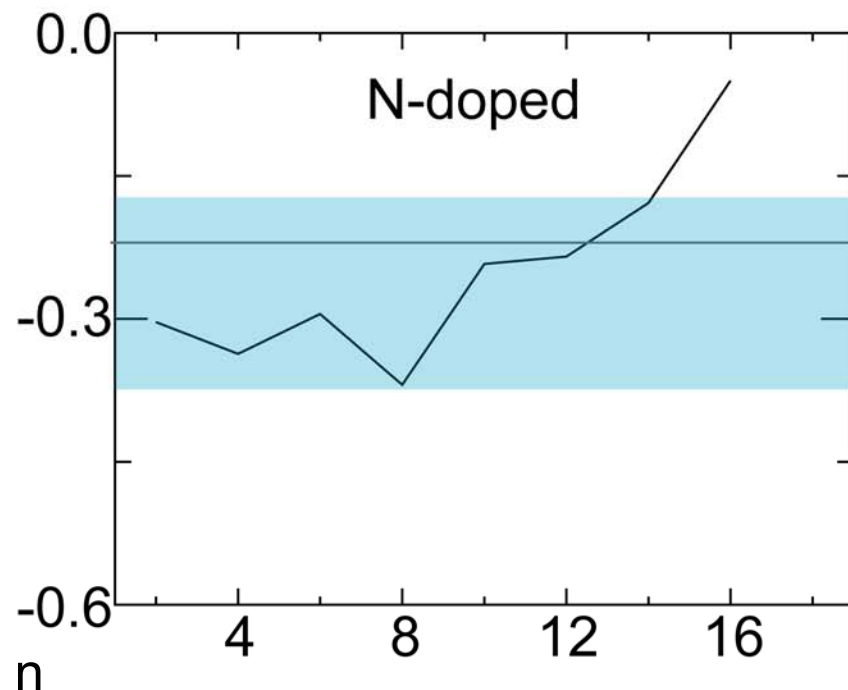
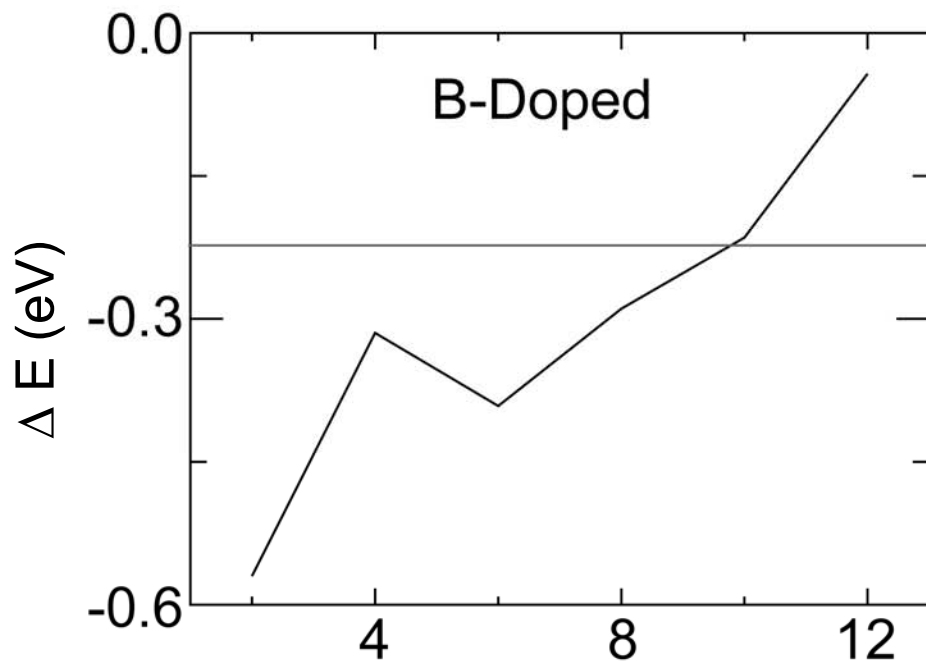
Spillover is possible at n > 12 after the adsorption of 7th H₂

Overall, less expensive Ni behaves similar to unsupported Pd as the same-column elements

Binding of metal cluster on graphene is weak and aggregation can be detrimental



Substituting one ring of **BN** gains little. Individually, both **B** or **N** doping strengthens the binding. Able to draw electrons from the metal cluster, **B is the best dopant-anchor, to ensure catalyst dispersion for efficient spillover** [R. Yang et al., Energy Environ. Sci., 2008, 1, 268]



B-doped

B doping has very little influence on the catalytic activity of metal
Threshold of spillover for B-doping remains unchanged

N-doped

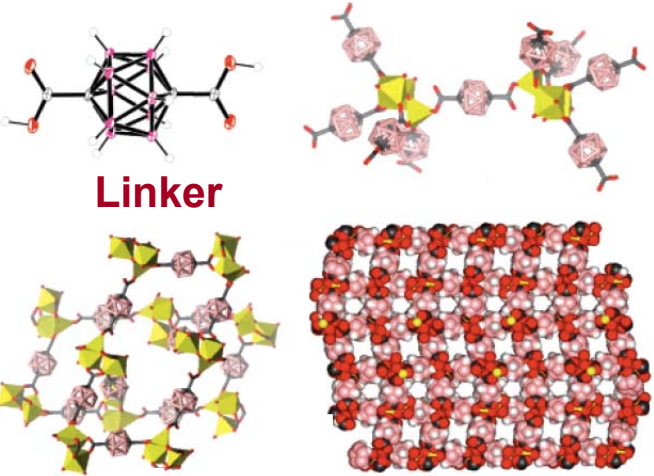
Threshold of spillover shifts to higher number of H₂

The binding energy of first H₂ is significantly reduced, and entropy-driven spillover can begin from the very first adsorbed H₂ (further improving the net capacity)

Towards metallocarborane based MOF

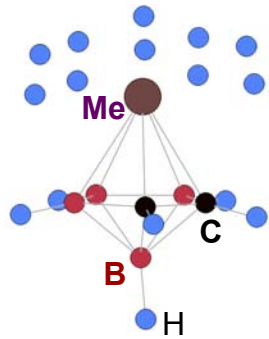
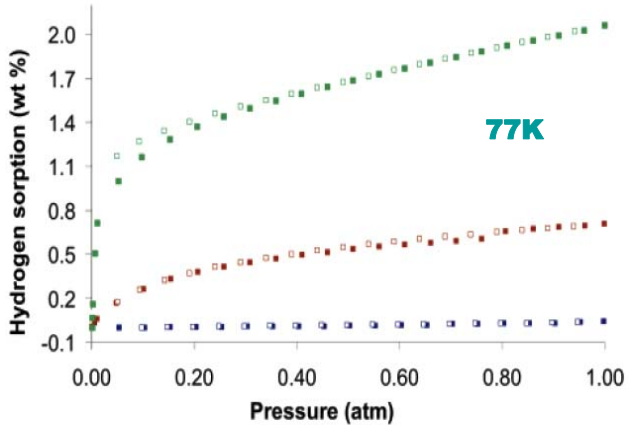
technical accomplishments 4

Farha *et al.* JACS 2007, 129, 12680

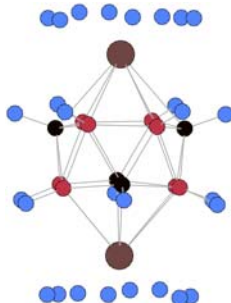


Linker

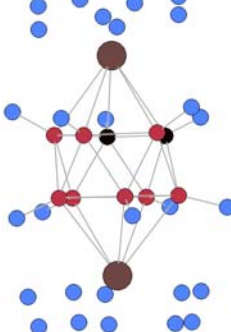
Replacing the linkers (on the right) with metallocarboranes enhances H₂ uptake



Metal	Wt. %	Binding eV
Sc	7.85	0.2~0.52
Ti	7.67	0.24~0.76



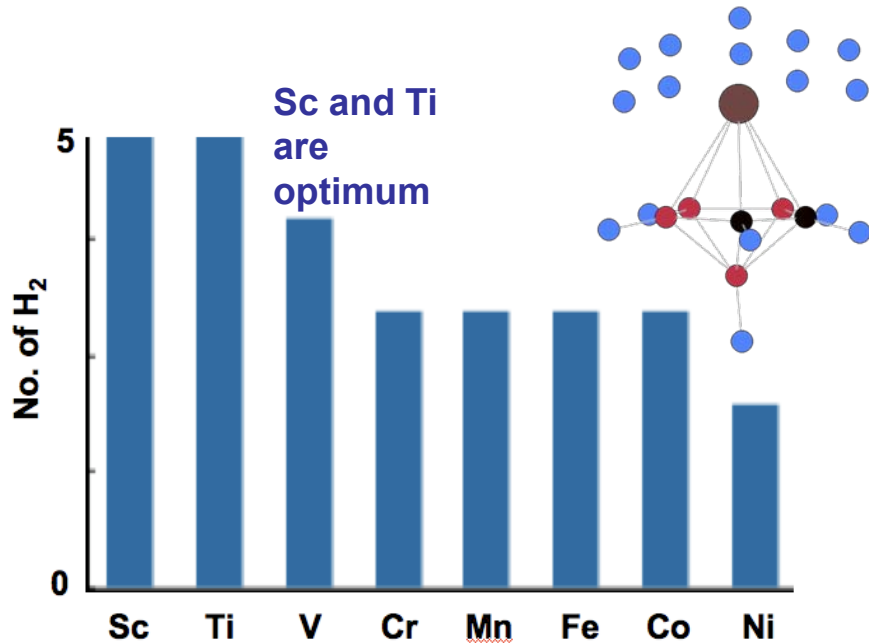
Sc	7.93	0.12~0.40
Ti	7.73	0.24~0.62



Sc	6.38	0.18~0.36
Ti	6.23	0.10~0.50

Search for an optimum transition metal for metallocarborane based MOF

Smallest B cluster considered for analysis



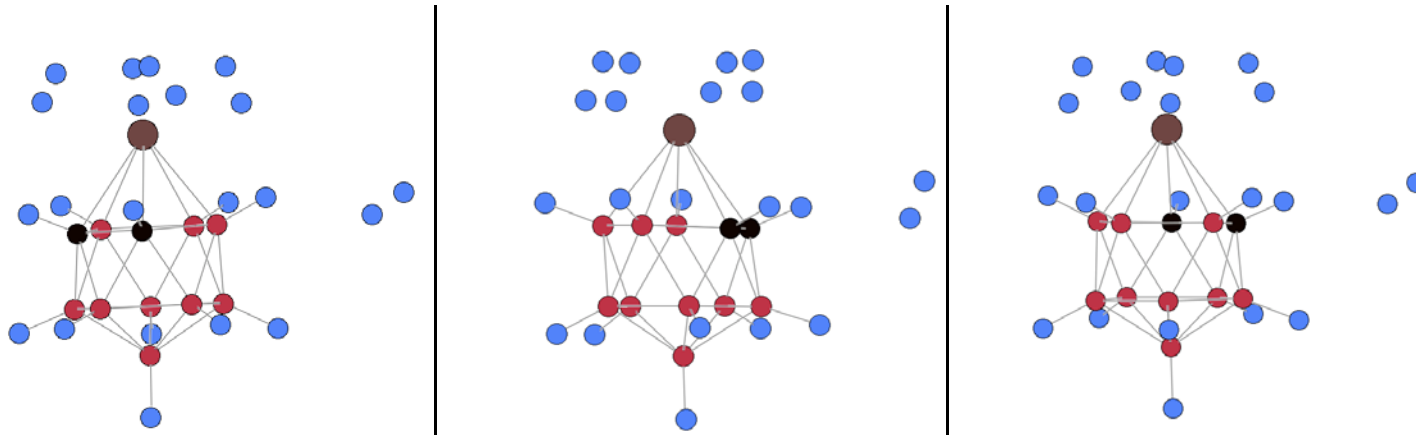
- Manifold increase in hydrogen uptake
- Me-centered capacity adds on top of the already measured for carborane-MOF
- Binding energies are optimal for reversible storage
- Two C available to be linked into the MOFs architecture

Number of H₂ adsorbed decreases with the increasing number of d electrons

The behavior is different from Cp (violation of 18e rule, being analyzed)

Binding strengths are in the range of reversible storage, making mcb-MOF promising H₂-storage media (~7%)

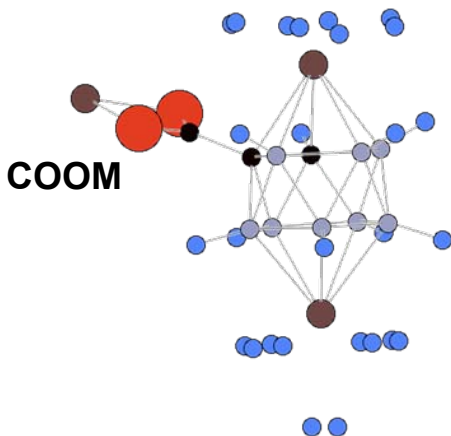
Adsorption of H₂ on the non-metal “surface” of the linker



Only physisorption for H₂ to the surface of the cluster

Three non equivalent adsorption sites on cluster considered

Effect of carboxylate link on the H₂ uptake



Storage capacity remains undiminished in MOF architecture.

Possibility of adsorbing additional H₂ on carboxylate metal is under consideration

Collaborations

Within the Center

Caltech – samples testing for H-storage capacity

U Michigan – comparison with available experiments, reciprocal visits

NIST – vibrational computations for spectroscopy signature of H-binding on carbon

Air Product, Inc. – nanotube scaffolds computations; spillover dynamics theory

NREL – exchange of ongoing results on boron-rich structures

Outside of the Center

Wright State University – Grand Canonical Monte Carlo simulations

Hong Kong Polytechnic University – spillover kinetics

ORNL – storage phase studies in spillover

University of Nevada Las Vegas – computations of scaffolds capacities

3D-foams

- 1. Use foams as model to quickly assess the storage capacity of carbon porous materials. Optimize both gravimetric and volumetric contents with respect to accessible surface area. Complete developing of the GCMC-evaluator and include the quantum corrections for more accurate realistic isotherm.

Metallacarboranes

- 2. Search for lighter metal atoms (e.g. Ca) to maximize the wt%. Effect of linkers on the wt and volume%. Optimize structures for metallacborane based MOFs

VANTA and AC chemical modifications

- 3. Conversion of nitrogen doped π -delocalized carbon systems such as giant fullerenes, VANTA, and AC, to superacid salts and test for hydrogen storage. High pressure FTIR studies of curvature dependent hydrogen spillover.

spillover dynamics

- 4. Study the effect of surface modification on the thermodynamics and kinetics of the spillover. Evaluations of effect of curvature size of metal cluster dopant, bridges on the migration barriers of H from activator to receptor. The possibility of transport of H atoms, as the recombination will be forbidden by the momentum conservation.
- Continue our work on dynamics of the chemically bound/absorbed hydrogen atoms: barriers and sigmatropic selection rules for H-hopping. Diffusion of H atom from catalyst to graphene and the rate of spread, quantitative front propagation model in contrast to conventional $\langle r^2 \rangle \sim D \times t$ diffusion.

Relevance: Path-finding to reach DOE goals by modeling of major options: sorption on *3D-foams, metal-enhancement, doping, spillover, B-based structures*.

Approach: Quantum ab initio and empirical representations of H-carriers interaction, to assess their retaining ability. Selectively test synthesis options.

Technical Accomplishments and Progress:

- 3D-foam has been optimized for the storage. The surface area of foams are evaluated. Quantum corrections are incorporated to estimate realistic storage capacities.
- Hydrogen uptake in metallocarboranes are studied. Capacities are closer to DOE goals.
- Efforts made towards optimizing the catalysts for spillover. B and N has emerged as good anchors for metal catalysts. N-doping is promising for enhancement of spillover kinetic.
- The barrier for H to move from metal to the hydrogenated phase is very small and can be overcome at room temperature.
- High surface area carbon converted to superacid salts and tested for enhanced hydrogen storage. So far no enhancement of hydrogen storage due to conversion to a superacid has been revealed.

Tech Transfer/Collaborations: Partnership with NREL, Air Products, NIST (spectroscopy), U Michigan and U Nevada Las Vegas, and Cal Tech.

Future Research: ● Complete foam-models for quick assessment of storage capacity ● Nitrogen doped carbon materials, large fullerenes and graphene sheets as high area superacid materials for hydrogen storage ● Emphasis on theory spillover dynamics, including other material-receptors (in collaboration with Yang's project). Proposed possible structures for metallocarboranes

Additional back-up slides

Impact across the Center

**Concept of 3D-foams proposed and computationally demonstrated –
Direct impact on Rice’s project (PI Tour), and beyond (UNLV).**

**Me atom aggregation issues addressed. –
Impacts all Kubas’ interaction based enhancement work (NREL, Rice, NIST).
Suggests special care and possible anchor-sites for Me attachments.**

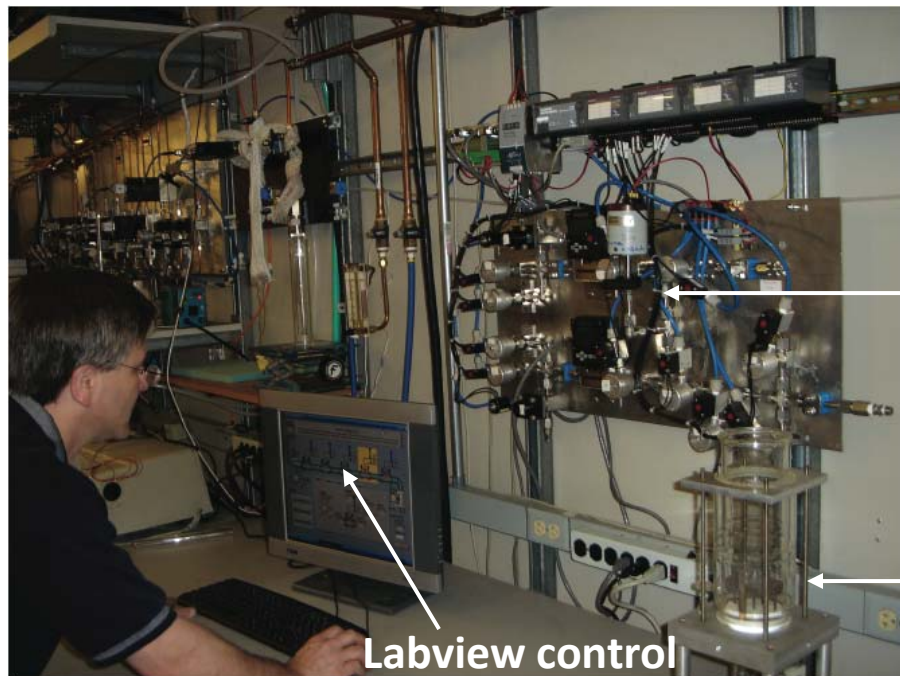
**Moreover, performed analysis can bridge *Kubas’ type enhancement*
with the *spillover function* on (aggregated) metal clusters.**

**VANTA synthesis and chemical enhancement offers material
for further processing for storage
by other center members (NREL, Air Products).**

**Spillover theory, after fundamental kinetics is understood,
should yield recommendations for better receptor and bridges design
(in collaboration with Center’s R Yang’s team at Michigan).**

**Miscellaneous: Computation of H vibration signatures assists
neutron-scattering diagnostics of spillover at NIST.**

System for synthesis of metal- and electro-negative-group- (F , BF_3) enhanced VANTA



Reaction system for generation of fullerene superacid boron tetrafluoride salts, to enhance H_2 polarization for storage

technical accomplishments 2

Parameters for best growth of VANTA scaffolds have been defined and VANTAs are now available for addition of electronegative groups for enhanced H_2 adsorption.

A variable temperature reactor has been built and tested for controlled exposure of samples to fluorine and boron trifluoride.

High surface area carbon samples supplied by Channing Ahn, Cal. Tech., have been converted to a carbon nanotube salt and tested for hydrogen uptake in collaboration with Channing Ahn

Vibration frequencies of chemically absorbed H atoms, computed for the Center's team at NIST, for n-scattering spillover diagnostics (localization signature)

